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(54) Title: BOULE OSCILLATION PATTERNS FOR PRODUCING FUSED SILICA GLASS

(57) Abstract

Oscillation/rotation patterns for improving the off axis homogeneity of fused silica boules are provided. The patterns reduce the optical effects of periodic off-axis striae by decreasing the ratio of Δn_{striae} to Δz_{striae}, where Δn_{striae} is the average peak-to-valley magnitude of the striae and Δz_{striae} is their average peak-to-peak period. The oscillation/rotation patterns have long repeat periods and cause soot-producing burners to trace out substantially spiral-shaped patterns on the surface of the boule.

5   BOULE OSCILLATION PATTERNS FOR PRODUCING
                              FUSED SILICA GLASS

       FIELD OF THE INVENTION
              This invention relates to the production of fused
10   silica glass and, in particular, to methods for improving
       the homogeneity of such glass, i.e., for reducing
       variations in the index of refraction of the glass.
       DESCRIPTION OF THE TECHNOLOGY
              Figure 1 shows a prior art furnace 10 for producing
15   fused silica glass. In overview, silicon-containing gas
       molecules are reacted in a flame to form SiO_2 soot
       particles. These particles are deposited on the hot
       surface of a rotating body where they consolidate into a
       very viscous fluid which is later cooled to the glassy
20   (solid) state. In the art, glass making procedures of
       this type are known as vapor phase hydrolysis/oxidation
       processes or simply as flame hydrolysis processes. The
       body formed by the deposited particles is often referred
       to as a "boule" and this terminology is used herein, it
25   being understood that the term includes any silica-
       containing body formed by a flame hydrolysis process.
              Furnace 10 includes a crown 12 having multiple
       deposition burners 14, a ring wall 16 which supports the
       crown, and a rotatable base 18 mounted on a x-y
30   oscillation table 20. The crown, ring wall, and base are
       each made of refractory materials.
              Refractory blocks 22 are mounted on base 18 to form
       containment vessel 13. The blocks form the vessel's
       containment wall and the portion of base 18 surrounded by
35   the wall (the bottom of the vessel) is covered with high
       purity bait sand 24 which collects the initial soot
       particles. Refractory blocks 22 can be composed of an

outer alumina base block 22a and an inner liner 22b made
of, for example, zirconia or zircon. Other refractory
materials and constructions can, of course, be used if
desired. A preferred construction for containment vessel
13, which is suitable for use with the present invention,
is described in commonly assigned U.S. patent application
Serial No. 60/003,608, entitled "Containment Vessel for
Producing Fused Silica Glass," which was filed on
September 12, 1995 in the name of John E. Maxon.

The space 26 between the top of containment vessel
13 and crown 12, which is referred to herein as a
"plenum", is vented by a plurality of vents 28 formed at
the top of ring wall 16 at its junction with the crown.
The vents are connected to a suitable exhaust system by
ducting which creates a negative pressure in the plenum.
The negative pressure causes air to flow upward through
annular gap 30 between the ring wall and the containment
vessel. A furnace system which controls for variations
in the air flow around the containment vessel and which
can be used in the practice of the present invention is
described in commonly assigned U.S. patent application
Serial No. 60/003,595, entitled "Furnace For Producing
Fused Silica Glass", which was filed on September 12,
1995 in the name of Paul M. Schermerhorn.

As practiced commercially, boules having diameters
on the order of five feet (1.5 meters) and thicknesses on
the order of 5-8 inches (13-20 cm) can be produced using
furnaces of the type shown in Figure 1. Multiple blanks
are cut from such boules and used to make various
products, including optical elements, such as, lenses
(including lenses for microlithography systems), prisms,
and the like. The blanks are generally cut in a
direction parallel to the axis of rotation of the boule
in furnace 10, and the optical axis of a lens element
made from such a blank will also generally be parallel to
the boule's axis of rotation. For ease of reference,
this direction will be referred to herein as the "z-

direction" or the "z-axis." Measurements of inhomogeneity made in a direction perpendicular to the z-axis will be referred to as "off-axis" measurements.

The amount of variation in the index of refraction of a blank which can be tolerated depends on the product which is to be made from the blank. Homogeneity of a blank or optical element is normally measured using interferometric techniques. When large parts are to be made, a large aperture interferometer is used, e.g., an interferometer having an aperture of 18 inches (46 cm).

Figure 2 shows an 17.3-inch (43.9 cm) interferometer plot (phase plot) for a fused silica boule prepared in accordance with the present invention. The boule was prepared using (1) a furnace of the type shown in Figure 1, (2) a containment vessel whose inner walls were sloped at an angle of 10° with respect to vertical, and (3) the oscillation/rotation pattern referred to below as "process 3".

Quantitatively, the z-direction homogeneity of a blank is expressed as its Δn value, which is calculated from the interferometer plot using the equation:

$$\Delta n = (\lambda \cdot PV) / t_b, \qquad (1)$$

where λ is the wavelength of light used by the interferometer, PV is the difference between the highest peak and the lowest valley of the phase plot, and t_b is the thickness of the blank. The homogeneity of a blank can also be expressed in other ways, such as in terms of the root-mean-square (RMS) deviation of the phase plot, which provides a measure of the variations in n between different points of the blank. See, for example, Japanese Patent Application Disclosure No. 6-308717, published November 4, 1994.

An application for fused silica blanks which requires very low values of Δn (e.g., Δn values less than or equal to 1.0×10^{-6} and preferably less than or equal to 0.5×10^{-6} for blanks having a diameter of 125 mm and

larger) is in the production of optical elements for microlithography systems.

Microlithography systems are used to produce integrated circuits and generally include a deep UV laser light source, an illumination lens system, and a projection (imaging) lens system. See, for example, Pfau et al., "Quartz inhomogeneity effects in diffraction-limited deep ultraviolet imaging," Applied Optics, Vol. 31, No. 31, pages 6658-6661 (November 1, 1992). The illumination lens system expands the laser beam and homogenizes its intensity. The projection lens system projects a very high resolution image of a mask onto a resist-covered IC wafer.

Diffraction effects limit the line width produced at the IC wafer and thus limit the density of circuits which can be written onto the wafer. In particular, the resolution (R) at the wafer is given by:

$$R = K \cdot \lambda_L / NA, \qquad (2)$$

where K is a constant whose value depends on the particular system and process used, λ_L is the operating wavelength of the laser light source, and NA is the numerical aperture of the projection lens system.

Reducing the wavelength of the laser light thus improves the resolution and allows narrower lines to be written on the wafer. Accordingly, in recent years, shorter wavelength lasers, e.g., lasers having a wavelength of 400 nm or less, have come into use in microlithography systems. Examples of such lasers include KrF and ArF excimer lasers which operate at 248 nm and 193 nm, respectively.

At these short (UV) wavelengths, standard optical glasses cannot be used for the optical elements of the system because of their high absorption. Fused silica glass, on the other hand, is transparent in the UV range and has thus become the material of choice for this application.

Because the goal of a microlithography system is to produce an image having a resolution in the submicron range, the lens elements used in such a system, and thus the lens blanks used to produce the lens elements, must

5   be of the highest quality. Among other properties, such lens blanks must have high internal transmission values, e.g., above about 99.8% ± 0.1% per centimeter, low levels of inclusions, low birefringence, low fluorescence, and high resistance to laser damage at UV wavelengths.

10   Of critical importance is the blank's Δn value since uncontrolled variations in n manifest themselves as uncorrectable aberrations in the image produced at the IC wafer. Moreover, from equation (2) above, to achieve high resolution, large NA values are needed. Large NA

15   values, in turn, mean large lens elements. Accordingly, not only must Δn be small, it must be small for large blank sizes.

Examples of the efforts which have been made to achieve this combination of a low Δn value and a large

20   blank size include Yamagata et al., U.S. Patent No. 5,086,352, PCT Publication No. WO 93/00307 published January 7, 1993, Japanese Patent Application Disclosure No. 5-116969 published May 14, 1993, Japanese Patent Application Disclosure No. 6-166527 published July 14,

25   1994, Japanese Patent Application Disclosure No. 6-234530 published August 23, 1994, and Japanese Patent Application Disclosure No. 6-234531 published August 23, 1994.

In addition to small Δn values for large blank

30   sizes, optical elements used in microlithography systems need to have high off-axis homogeneity, again for large blank sizes. See, for example, Japanese Patent Application Disclosure No. 5-97452, published April 20, 1993, which discusses the need for homogeneity in three

35   directions. This is especially important for prismatic elements used in such systems, where optical planes are

formed at angles relative to a blank's z-direction. (See
the Pfau et al. article cited above; note that off-axis
homogeneity is also important for prisms and other
optical elements used in applications other than
microlithography systems.)

Off-axis homogeneity can be observed and/or measured
in various ways, including through the use of a
shadowgram in which diverging light from a point source
is passed through a sample and the resulting pattern is
observed on an observation screen and through
diffraction-based techniques where collimated light is
passed through a sample and the far-field diffraction
pattern is observed in the Fourier transform plane of a
long focal length lens (see "Corning Tests for Striae in
Fused Silica," Laser Focus World, page 110, August 1993).

A preferred method for measuring off-axis
inhomogeneity is by means of an interferometer/camera
system which has a sufficiently fine spatial resolution
to detect the inhomogeneities of interest, e.g., a
spatial resolution of 18-20 pixels/mm of glass. Such
resolution can be achieved by employing a high resolution
camera or through the use of a beam reducer located
between the interferometer and the sample, this latter
approach having the disadvantage that only a small
portion of a blank or optical element can be examined at
a time. To distinguish off-axis inhomogeneities from
noise, processing of the interferometer signal can be
performed in accordance with the techniques described in
commonly assigned U.S. patent application Serial No.
60/003,607, entitled "Methods for Detecting Striae",
which was filed on September 12, 1995 in the names of
David R. Fladd and Stephen J. Rieks.

Using procedures of the foregoing type, off-axis
inhomogeneities in the form of periodic (sinusoidal)
striae have been observed for blanks made using furnaces
of the type shown in Figure 1. Figure 3 is an off-axis
phase plot for a blank prepared using a prior art

oscillation/rotation pattern and a furnace of the type shown in Figure 1. A strong periodic off-axis inhomogeneity having an average peak-to-peak period of about a half a millimeter can be clearly seen in this figure.

Quantitatively, such striae have been found to have δn values around 10×10^{-8}, where

$$\delta n = (\lambda \cdot PV) / PL, \qquad (3)$$

λ is the wavelength of light used by the interferometer, PV is the difference between the highest peak and the lowest valley of the phase plot produced by the interferometer for the striae, and PL is the off-axis path length through the blank.

The present invention is directed to reducing this off-axis inhomogeneity, while at the same time maintaining a high level of homogeneity in the z-direction. In particular, the invention is directed to increasing the average peak-to-peak period (spacing) of the striae (Δz_{striae}), as well as to reducing their average peak-to-valley magnitude (Δn_{striae}) at least to some extent. In this way, the ratio of these average values, i.e., the $\Delta n_{striae}/\Delta z_{striae}$ ratio, can be decreased, which reduces the optical effects of the striae.

SUMMARY OF THE INVENTION

In view of the foregoing, it is an object of this invention to provide improved methods for producing silica-containing boules by the flame hydrolysis process. In particular, it is an object of the invention to improve the off-axis homogeneity of such boules and thus the off-axis homogeneity of blanks and optical elements, including prisms and lens elements, made therefrom. It is a further object of the invention to provide blanks and optical elements which have a high off-axis homogeneity, a high z-axis homogeneity, and a large size.

In accordance with the invention, it has been discovered that the off-axis homogeneity of a boule, and thus the off-axis homogeneity of blanks and optical elements made therefrom, depends upon two aspects of the oscillation pattern used to produce the boule.

The first aspect is the repeat period of the oscillation pattern, i.e., the period of time it takes for the boule to return to substantially the same place in the furnace going in substantially the same direction at substantially the same speed. In accordance with the invention, it has been found that Δz_{striae}, as measured interferometrically, is substantially linearly related to the repeat period. That is, as the repeat period increases, Δz_{striae} increases. An increase in Δz_{striae}, in turn, means a decrease in the $\Delta n_{striae}/\Delta z_{striae}$ ratio, which, as discussed above, means that the optical effects of the striae are reduced.

In particular, it has been found that off-axis periodic striae can be significantly reduced if oscillation patterns having repeat periods greater than about 8 minutes and preferably about 10 minutes are used in the boule preparation process.

It has been further found that there is a substantial difference between the physical amount of glass deposited during a repeat period and the observed Δz_{striae}. That is, Δz_{striae} is on the order of 10-15 times greater than the thickness of glass deposited during the repeat period. In accordance with this aspect of the invention, the repeat period of the oscillation pattern is chosen so as to correspond to the deposition of at least about 0.15 mm of glass and preferably about 0.20 mm of glass.

The second aspect of the oscillation pattern which affects off-axis periodic striae is the pattern's relationship to the overall rotation of the boule relative to the furnace's burners. In accordance with

the invention, it has been found that periodic off-axis striae can be substantially reduced if the oscillation pattern and the overall rotation rate are selected so that burners traverse substantially spiral paths over the boule.

In accordance with this aspect of the invention, it has been further found that the use of a pure spiral reduces off-axis striae but at the expense of z-axis homogeneity. Accordingly, in accordance with certain preferred embodiments of the invention, the spiral paths are given at least some wobble to hold Δn within acceptable limits (such paths are referred to herein as "substantially spiral paths" or as "spiral-like paths"). In addition, the processing conditions and containment vessel described in the above referenced application entitled "Containment Vessel for Producing Fused Silica Glass" can be used with the spiral or spiral-like patterns to provide the requisite level of z-axis homogeneity. In general terms, the methods and apparatus of that application provide for:

(1) maintaining a sufficiently high boule temperature during the boule formation process so that the boule will flow radially under its own weight with a minimum of head height, specifically, with a head height less than or equal to about 5.0 mm and preferably less than or equal to about 0.125 inches (3.2 mm) of glass;

(2) forming the boule in a containment vessel whose inner radius r_v is substantially larger than the radius r_b of the outermost of the deposition burners used to form the boule, e.g., the ratio of r_v to r_b is at least about 1.1; and/or

(3) forming the boule in a containment vessel having an inner containment wall or walls whose vertical height h increases with increasing

distance d from the center of the vessel at a
rate $\Delta h/\Delta d$ which is less than or equal to about
3.

By means of the invention, blanks and optical
elements can be produced having $\Delta n_{striae}/\Delta z_{striae}$ values
less than or equal to about 2.0×10^{-8} mm^{-1} and preferably
less than or equal to about 1.5×10^{-8} mm^{-1}, and z-axis
homogeneity values (Δn values) less than or equal to 1.0
$\times 10^{-6}$ and preferably less than or equal to 0.5×10^{-6} for
blank (element) sizes (e.g., diameters for cylindrical
blanks) greater than or equal to 125 mm, preferably
greater than or equal to 150 mm, and most preferably
greater than or equal to 200 mm. To achieve z-axis
homogeneity values of 0.5×10^{-6} or less, the apparatus
and methods of the above referenced application entitled
"Containment Vessel for Producing Fused Silica Glass"
will generally be needed. Depending upon the
capabilities of the testing equipment used, satisfaction
of the $\Delta n_{striae}/\Delta z_{striae}$ and the Δn criteria can be
determined by testing the blank or element as a whole or
by testing representative sections thereof. Values for
the $\Delta n_{striae}/\Delta z_{striae}$ ratio can be determined manually or
automatically by computer using a phase plot or
preferably a profile line derived therefrom. See the
above-referenced application entitled "Methods for
Detecting Striae" and, in particular, the discussion of
Figure 11 of that application.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of a prior art
furnace used to produce fused silica boules using a flame
hydrolysis process.

Figure 2 shows an 17.3-inch (43.9 cm) interferometer
phase plot for a section of a fused silica boule prepared
in accordance with the present invention. The phase plot
is taken along the z-axis of the boule. As shown, the
PST, TLT, and PWR components have been removed from the

original raw data (ZYGO terminology; Zygo Corporation, Middlefield, CT).

Figures 3, 4, and 5 are off-axis phase plots for blanks prepared using prior art furnaces of the type shown in Figure 1 and containment vessels whose inner walls were sloped at an angle of 10° with respect to vertical. The boule oscillation and rotation parameters used in preparing these blanks are those referred to in Table 1 as process 1 (Figure 3), process 2 (Figure 4), and process 3 (Figure 5). The phase plots of these figures were prepared using a beam reducer between the interferometer and the sample and thus have an aperture of only about 6.5 mm. The data analysis procedures of the above-referenced application entitled "Methods for Detecting Striae" were not used in the preparation of these plots. As shown, the PST and TLT components have been removed from the raw data for each of these figures.

It should be noted that the vertical scales in Figure 2 on the one hand and Figures 3, 4, and 5, on the other hand, are different, as are the horizontal scales; in particular, Figures 3, 4, and 5 have expanded scales in both the vertical and horizontal direction as compared to Figure 2.

Figures 6A, 7A, and 8A are plots of x(t) versus t for processes 1, 2, and 3, respectively. Figures 6B, 7B, and 8B are plots of y(t) versus t, again for processes 1, 2, and 3, respectively.

Figures 9A, 10A, and 11A are "spirograms" for processes 1, 2, and 3, respectively, at 300 seconds. Figures 9B, 10B, and 11B are the corresponding spirograms at 700 seconds.

Figure 12 is a schematic diagram of the burner locations used in producing Figures 9-11.

The foregoing drawings, which are incorporated in and constitute part of the specification, illustrate the preferred embodiments of the invention, and together with the description, serve to explain the principles of the

invention. It is to be understood, of course, that both the drawings and the description are explanatory only and are not restrictive of the invention.

The drawing of Figure 1 is not intended to indicate scale or relative proportions of the elements shown therein.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As discussed above, the present invention relates to methods for improving the homogeneity of silica-containing bodies made by vapor deposition techniques. The silica-containing body can be substantially pure fused silica or can contain one or more dopants as desired, e.g., the body can contain a titanium dopant which lowers the coefficient of thermal expansion of the glass. Low levels of contaminates may also be present in the body.

In accordance with the invention, improved off-axis homogeneity is achieved by means of the oscillation/rotation pattern used during the formation of the boule. The particular patterns used in the experiments reported herein were defined by the following equations:

$$x(t) = r_1 \sin 2\pi\omega_1 t + r_2 \sin 2\pi\omega_2 t \quad (4)$$

$$y(t) = r_1 \cos 2\pi\omega_1 t + r_2 \cos 2\pi\omega_2 t \quad (5)$$

where $x(t)$ and $y(t)$ represent the coordinates of the center of the boule as measured from the center of ringwall 16 as a function of time (t) and time is measured in minutes. This geometry is schematically illustrated in Figure 12, where 100 represents the center of the ringwall and 200 represents the center of the boule. It should be noted that the sum of r_1 and r_2 must be less than the difference between the radius of the ringwall and the radius of the containment vessel to avoid contact between these structures during formation of the boule.

In addition to the four parameters r_1, r_2, ω_1, and ω_2, the overall motion of the boule is also defined by a fifth parameter, ω_3, which represents the boule's rotation rate about its center in revolutions per minute (rpm). This overall rotation of the boule is illustrated by reference number 3 in Figure 1.

It should be noted that oscillation patterns that are more or less complex than those defined by equations (4) and (5) can be used in the practice of the invention, if desired. In particular, more than two frequencies can be used to define $x(t)$ and/or $y(t)$.

Table 1 sets forth three sets of values for r_1, r_2, ω_1, ω_2, and ω_3 which illustrate the features of the invention. For convenience, these sets of values will be referred to as "process 1", "process 2", and "process 3". Processes 1 and 2 are patterns that were used in the prior art, while process 3 follows the teachings of the present invention. The values in Table 1 are suitable for producing a boule having a diameter of about five feet (1.5 m). Suitable values for producing larger or smaller boules can be readily determined by persons skilled in the art from the disclosure herein.

As discussed above, in accordance with certain aspects of the invention, it has been found that the optical effects of periodic off-axis striae can be reduced by using an oscillation pattern having a sufficiently long repeat period. The repeat period can be determined from $x(t)$ and/or $y(t)$ versus time plots of the type shown in Figures 6-8.

Figure 6 shows the patterns obtained when $\omega_1 < \omega_2$; Figure 7 shows the case of $\omega_1 \sim \omega_2$; and Figure 8 shows the case of $\omega_1 \ll \omega_2$.

An examination of, for example, Figure 6A shows that at $t=0$ and again at about $t=120$ seconds, $x(t)$ is at its maximum. This maximum corresponds to $\sin 2\pi\omega_1 t$ and $\sin 2\pi\omega_2 t$ both being equal to or approximately equal to +1,

which occurs when the arguments of these sin functions are each substantially equal to $2n\pi$, n being different for ω_1 and ω_2. In particular, maximums of $x(t)$ occur whenever ω_1/ω_2 is substantially equal to n_1/n_2.

The maximum for t around 120 seconds corresponds to $n_1 = 3$ and $n_2 = 7$. This maximum occurs at approximately 2.1 minutes (126 seconds) where $2\pi\omega_2 t = 14\pi$ and $2\pi\omega_1 t = 6\pi$. The repeat period for process 1 is thus approximately 2.1 minutes.

The tracings of Figure 7 show a classical beat pattern, having a beat frequency equal to the magnitude of the difference between ω_2 and ω_1. The beat period is simply one over the beat frequency. Accordingly, the repeat period when $\omega_1 \approx \omega_2$ is simply $1/|\omega_2 - \omega_1|$. For the process 2 parameters of Table 1, the repeat period is approximately 4.9 minutes (294 seconds).

The tracings of Figure 8 illustrate the case where $\omega_1 << \omega_2$. For this condition, the repeat period is substantially the same as the period of the slower oscillation, i.e., the repeat period is approximately $1/\omega_1$. For the process 3 parameters of Table 1, the repeat period is thus approximately 10 minutes (600 seconds).

As discussed above, in accordance with the invention it has been found that the optical effects of periodic striae can be reduced by using a repeat period of at least about 8 minutes. It should be noted that such a repeat period can be achieved for any of the ω_1 to ω_2 relationships illustrated in Figures 6, 7, and 8, although the relationship of Figure 8, i.e., $\omega_1 << \omega_2$, is preferred. Similarly, the desired repeat period can be achieved for oscillation patterns whose composition is other than two sinusoidal waves.

In addition to being dependent upon the repeat period of the oscillation pattern, the off-axis periodic striae are also dependent upon the relationship between

the oscillation pattern and the overall rotation of the boule about its center. In particular, it has been found that off-axis periodic striae can be significantly reduced if the oscillation pattern and the boule's rotation rate are selected so that the paths which the burners trace across the surface of the boule are spirals.

A set of ω's and r's which is suitable for use in producing a boule which has a diameter of about five feet (1.5 m) and which produce such a spiral pattern is as follows: r_1 = 0; r_2 = 2.5 inches (6.35 cm); ω_1 = 0 rpm; ω_2 = 0.45 rpm; and ω_3 = 6.0 rpm. Note that ω_3 is greater than ω_2 as is required to produce a spiral path on the boule. Suitable values for producing larger or smaller boules can be readily determined by persons skilled in the art from the present disclosure.

Although a spiral pattern is effective in dealing with off-axis periodic striae, it has the disadvantage that it tends to produce relatively large Δn values. In accordance with the preferred embodiments of the invention, this problem is addressed by using burner paths which are substantially spirals, but not pure spirals. The parameters of process 3 produce such spiral-like burner patterns.

Figure 11 shows calculated laydown patterns for the process 3 parameters for three burners located near to the center 100 of ringwall 16. The relative locations of these burners are shown in Figure 12. Their radial distances from center 100 are 2.75 inches (7.0 cm) for burner 1, 5.00 inches (12.7 cm) for burner 2, and 6.63 inches (16.8 cm) for burner 3. Figure 11A shows the pattern at 300 seconds, while Figure 11B shows it at 700 seconds. The spiral-like nature of the burner paths is evident in these figures.

For comparison, Figures 9 and 10 show calculated laydown patterns for the same burner locations when

processes 1 and 2 are used. As these figures demonstrate, these processes result in patterns which are not spiral-like, but rather are highly reentrant, i.e., the burner's path crosses and recrosses itself as the
5   pattern develops.

Table 2 and Figures 3 (process 1), 4 (process 2), and 5 (process 3) illustrate the significant improvement in off-axis periodic striae achieved by the present invention. As shown therein, process 3 results in a
10   significantly lower $\Delta n_{striae}/\Delta z_{striae}$ value than either process 1 or process 2. The reduction in this value means that the optical effects of the striae are substantially reduced.

For example, in the shadowgram test in which
15   diverging light is passed through a sample and the resulting pattern is observed on a screen, samples prepared using process 1 produced easily visible parallel lines of high contrast on the screen and those prepared using process 2 produced slightly visible parallel lines
20   of low contrast. Process 3, on the other hand, produced samples for which the pattern on the screen was nearly invisible, which is the goal.

As discussed above, it has been found that there is a substantial difference between the observed Δz_{striae} and
25   the physical amount of glass deposited during a repeat period. Although not visible in the phase plots of Figures 3-5, the underlying structure of the glass which produces the periodic striae of those plots can be seen using the shadowgram technique. Specifically, movement
30   of a sample away from the shadowgram's light source to a position close to the shadowgram's screen has been found to cause a pattern to appear on the screen having a spatial frequency much higher than that observed when the sample is close to the light source. Although not
35   wishing to be bound by any particular theory of operation, it is believed that this finer pattern

corresponds to the fine structure of the glass which causes the periodic striae observed in the phase plots.

By means of the invention, significant improvements in homogeneity and off-axis homogeneity have been

5 achieved. For example, using process 3 and the apparatus and methods of the above-referenced application entitled "Containment Vessel for Producing Fused Silica Glass," boules having a diameter of up to 1.53 meters can be manufactured and used to produce blanks having diameters

10 up to 360 millimeters, Δn values of less than 0.5×10^{-6}, and $\Delta n_{striae}/\Delta z_{striae}$ values less than 1.5×10^{-8} mm^{-1}. Such blanks can be used to produce optical elements for microlithography systems employing, for example, KrF lasers.

15 Although specific embodiments of the invention have been described and illustrated, it is to be understood that modifications can be made without departing from the invention's spirit and scope. For example, although the invention has been described in terms of stationary

20 burners and a moving boule, it is the relative motion between the source of the soot particles and the boule which is important. Accordingly, in addition to using a stationary source and a moving boule as described above (the preferred approach), the required motion can also be

25 achieved by holding the boule stationary and moving the soot particle source or by moving both the boule and the soot particle source.

A variety of other modifications which do not depart from the scope and spirit of the invention will be

30 evident to persons of ordinary skill in the art from the disclosure herein. The following claims are intended to cover the specific embodiments set forth herein as well as such modifications, variations, and equivalents.

TABLE 1

	r_1 inches (cm)	r_2 inches (cm)	ω_1 (rpm)	ω_2 (rpm)	ω_3 (rpm)
Process 1	1.0 (2.54)	1.5 (3.81)	1.4375	3.354	4.04615
Process 2	1.0 (2.54)	1.5 (3.81)	5.3046	5.09852	6.7018
Process 3	0.6 (1.52)	1.9 (4.83)	0.1	0.41	6.9

TABLE 2

	PV	PL (mm)	Δn_{striae}	Δz_{striae} (mm)	$\Delta n_{striae}/\Delta z_{striae}$ (mm^{-1})
Process 1	0.015	180.6	5.2×10^{-8}	0.560	9.29×10^{-8}
Process 2	0.017	169.8	6.3×10^{-8}	1.710	3.68×10^{-8}
Process 3	0.015	232.9	4.1×10^{-8}	2.997	1.37×10^{-8}

What is claimed is:

1.   A method for forming a silica-containing body comprising:

(a)   providing a source of soot particles;

(b)   collecting the soot particles to form the body, said collection causing the thickness of the body to increase; and

(c)   providing relative oscillatory motion between the source and the body as the soot particles are collected, said oscillatory motion being orthogonal to the thickness of the body and having a repeat period;

said collection and oscillation being performed so that the thickness of the body increases by at least about 0.15 mm during the repeat period.

2.   The method of Claim 1 wherein the thickness of the body increases by at least about 0.2 mm during the repeat period.

3.   A method for forming a silica-containing body comprising:

(a)   providing a source of soot particles;

(b)   collecting the soot particles to form the body, said collection causing the thickness of the body to increase; and

(c)   providing relative oscillatory motion between the source and the body as the soot particles are collected, said oscillatory motion being orthogonal to the thickness of the body and having a repeat period of at least about eight minutes.

4.   The method of Claim 3 wherein the repeat period is about 10 minutes.

5.   A method for forming a silica-containing body comprising:

(a)   providing a source of soot particles;

(b)   collecting the soot particles to form the body, said collection causing the thickness of the body to increase; and

(c) rotating the body and providing relative oscillatory motion between the source and the body as the soot particles are collected, said oscillatory motion being orthogonal to the thickness of the body and said rotation and oscillatory motion being such that the projection of the source onto the body traces out a path which is substantially a spiral.

6. The method of Claim 5 wherein the path is a pure spiral.

7. The method of Claim 5 wherein the source comprises a plurality of soot producing burners and each burner traces out a path which is substantially a spiral.

8. The method of Claim 5 wherein the oscillatory motion has a repeat period and the collection and oscillation are performed so that the thickness of the body increases by at least about 0.15 mm during the repeat period.

9. The method of Claim 8 wherein the thickness of the body increases by at least about 0.2 mm during the repeat period.

10. The method of Claim 5 wherein the oscillatory motion has a repeat period of at least about eight minutes.

11. The method of Claim 10 wherein the repeat period is about 10 minutes.

12. A silica-containing body made by the method of Claim 1, 3, or 5.

13. The silica-containing body of Claim 12 wherein the body contains a dopant.

14. A blank made from the silica-containing body of Claim 12.

15. An optical element made from the blank of Claim 14.

16. A method for reducing off-axis periodic striae in the index of refraction of a blank formed from a silica-containing body, said striae having an average

peak-to-valley magnitude Δn_{striae} and an average peak-to-peak period Δz_{striae}, said method comprising:

    (a)   providing a source of soot particles;

    (b)   collecting the soot particles to form the body, said collection causing the thickness of the body to increase; and

    (c)   providing relative oscillatory motion between the source and the body as the soot particles are collected, said oscillatory motion being orthogonal to the thickness of the body and having a repeat period which is sufficiently long so that $\Delta n_{striae}/\Delta z_{striae}$ for the blank is less than or equal to about 2.0×10^{-8} mm^{-1}.

17.   The method of Claim 16 wherein the repeat period is sufficiently long so that $\Delta n_{striae}/\Delta z_{striae}$ for the blank is less than or equal to about 1.5×10^{-8} mm^{-1}.

18.   The method of Claim 16 wherein the blank has a z-axis homogeneity Δn which is less than or equal to 1.0×10^{-6} for a blank size greater than or equal to 125 millimeters.

19.   The method of Claim 17 wherein the blank has a z-axis homogeneity Δn which is less than or equal to 1.0×10^{-6} for a blank size greater than or equal to 125 millimeters.

20.   The method of Claim 16 wherein the blank has a z-axis homogeneity Δn which is less than or equal to 0.5×10^{-6} for a blank size greater than or equal to 125 millimeters.

21.   The method of Claim 17 wherein the blank has a z-axis homogeneity Δn which is less than or equal to 0.5×10^{-6} for a blank size greater than or equal to 125 millimeters.

22.   The method of Claim 18, 19, 20, or 21 wherein the blank size is greater than or equal to 150 millimeters.

23. The method of Claim 18, 19, 20, or 21 wherein the blank size is greater than or equal to 200 millimeters.

24. The method of Claim 16 wherein the body is rotated and the rotation and the oscillatory motion causes the projection of the source onto the body to trace out a path which is substantially a spiral.

25. The method of Claim 24 wherein the path is a pure spiral.

26. The method of Claim 24 wherein the source comprises a plurality of soot producing burners and each burner traces out a path which is substantially a spiral.

27. A blank made by the method of Claim 16.

28. The blank of Claim 27 wherein the blank contains a dopant.

29. An optical element made from the blank of Claim 27.

30. A fused silica blank which has:

(a) a $\Delta n_{striae}/\Delta z_{striae}$ value which is less than or equal to about 2.0×10^{-8} mm^{-1}, where Δn_{striae} and Δz_{striae} are the average peak-to-valley magnitude and the average peak-to-peak period, respectively, of the blank's off-axis striae; and

(b) a z-axis homogeneity Δn which is less than or equal to 1.0×10^{-6} for a blank size greater than or equal to 125 millimeters.

31. The fused silica blank of Claim 30 wherein the blank's $\Delta n_{striae}/\Delta z_{striae}$ value is less than or equal to about 1.5×10^{-8} mm^{-1}.

32. The fused silica blank of Claim 30 wherein the blank has a z-axis homogeneity Δn which is less than or equal to 0.5×10^{-6} for a blank size greater than or equal to 125 millimeters.

33. The fused silica blank of Claim 31 wherein the blank has a z-axis homogeneity Δn which is less than or

equal to 0.5 x 10^{-6} for a blank size greater than or equal to 125 millimeters.

34. The fused silica blank of Claim 30, 31, 32 or 33 wherein the blank size is greater than or equal to 150 millimeters.

35. The fused silica blank of Claim 30, 31, 32 or 33 wherein the blank size is greater than or equal to 200 millimeters.

36. An optical element made from the blank of Claim 30.

37. A lens element made from the blank of Claim 30.

38. A prism made from the blank of Claim 30.

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FIG. 1

PRIOR ART

+0.1364

WAVE

−0.0990

15.55

in

0.80

1.91   in   19.21
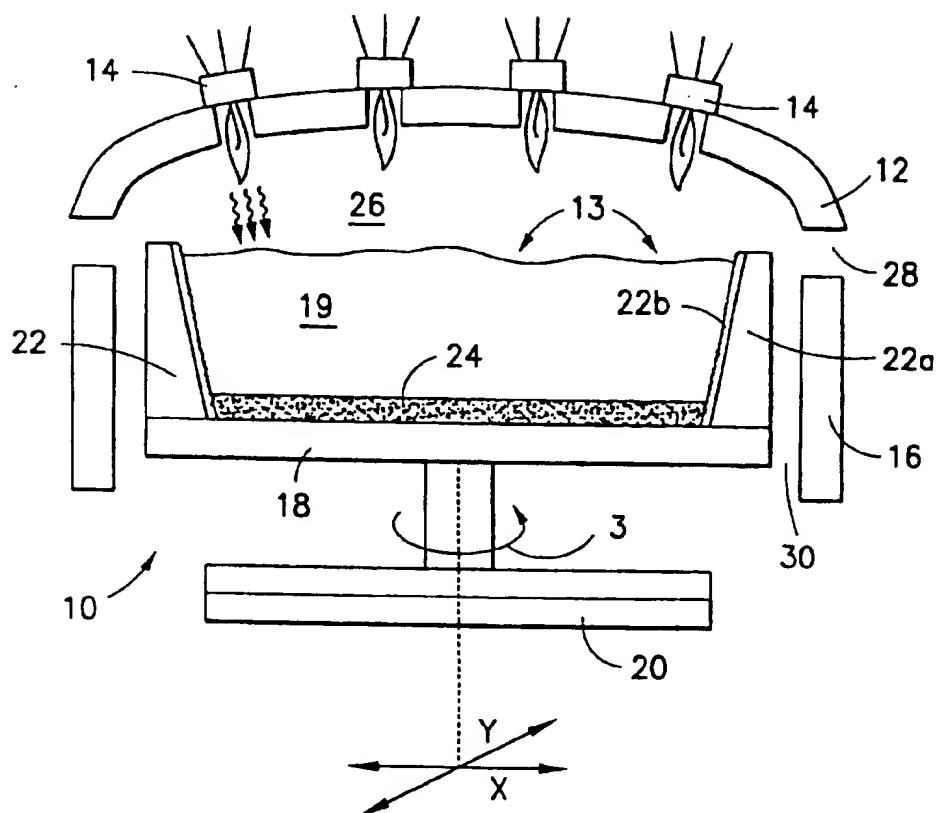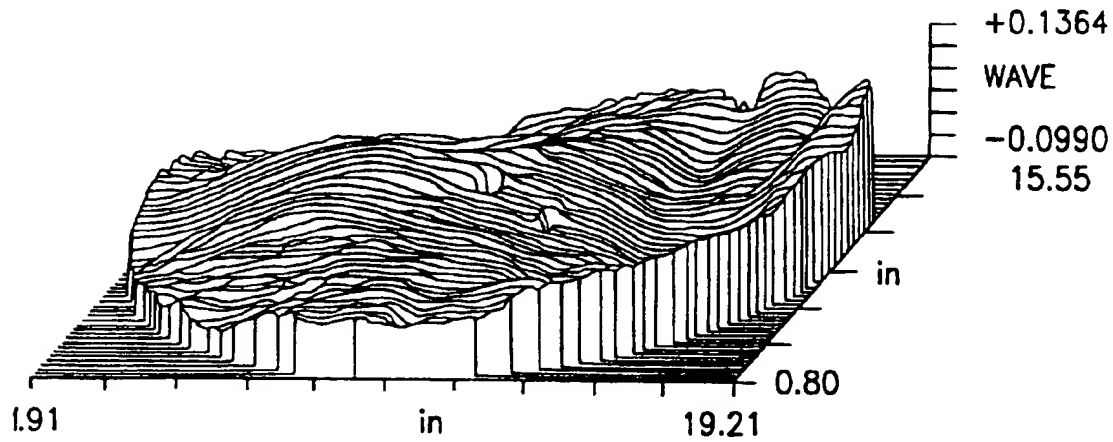
FIG. 2

PV	0.235 WAVES
RMS	0.040 WAVES
Δn	1.4×10^{-6}
THICKNESS	4.210" (10.7cm)
APERTURE	17.3" (43.9cm)
λ	632.8nm

+0.0153

WAVE

−0.0140

10.10

mm

3.59

3.83   mm   10.34
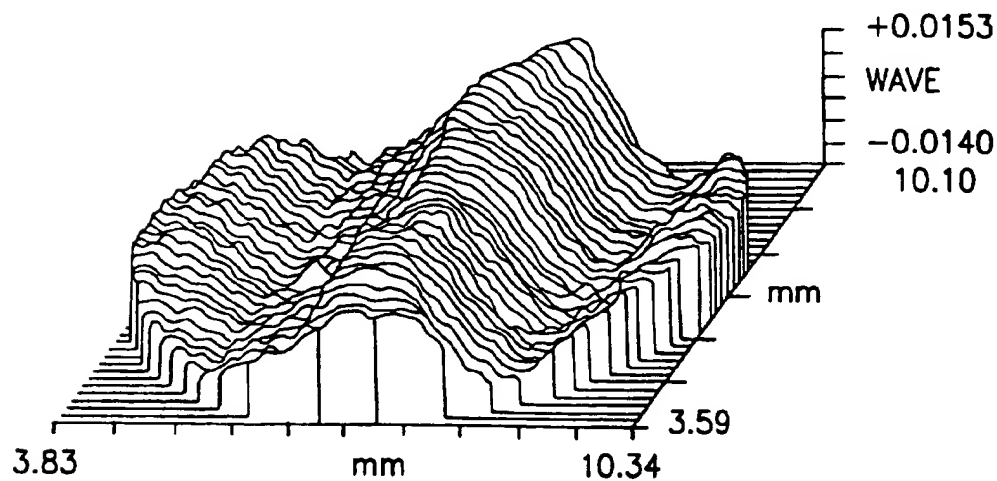
FIG. 5

PV	0.029 WAVES
RMS	0.007 WAVES
δn	7.96×10^{-8}
THICKNESS	9.17" (23.3cm)
APERTURE	6.51mm
λ	632.8nm

+0.0121

WAVE

−0.0135

6.70

mm

0.18

7.08

0.59   mm
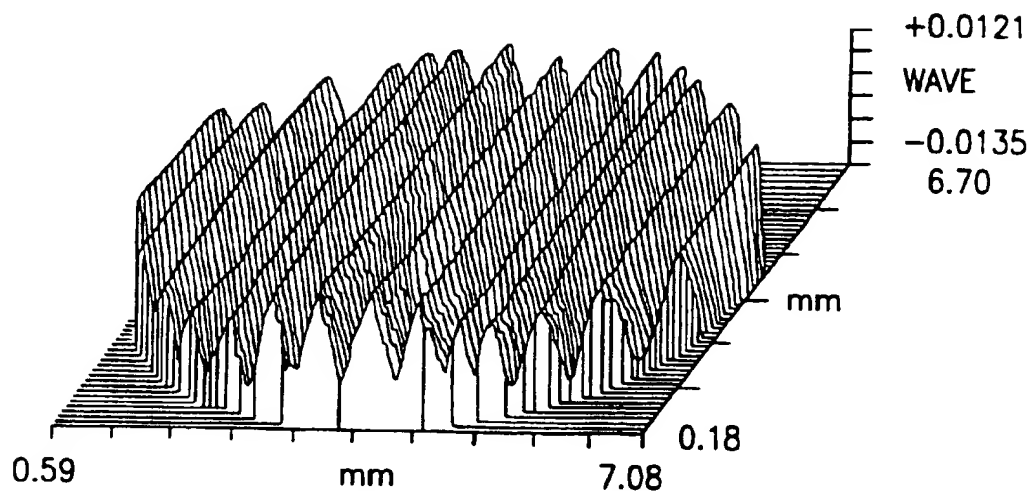
FIG. 3
PRIOR ART

PV	0.0256 WAVES
RMS	0.0058 WAVES
δn	8.98×10^{-8}
THICKNESS	7.11" (18.1cm)
APERTURE	6.49mm
λ	632.8nm

+0.0145

WAVE

−0.0137

6.70

mm

0.18

7.08

0.59   mm
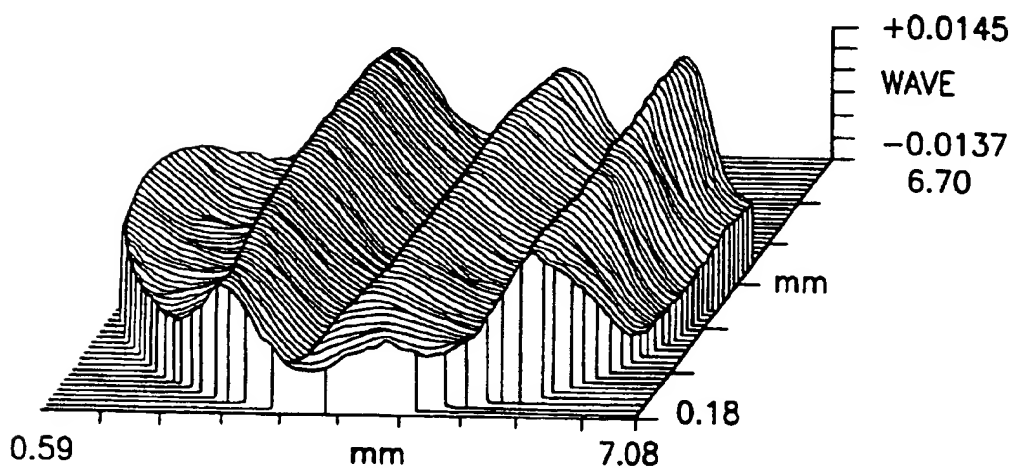
FIG. 4
PRIOR ART

PV	0.0282 WAVES
RMS	0.0057 WAVES
δn	1.05×10^{-7}
THICKNESS	6.685" (17cm)
APERTURE	6.49mm
λ	632.8nm
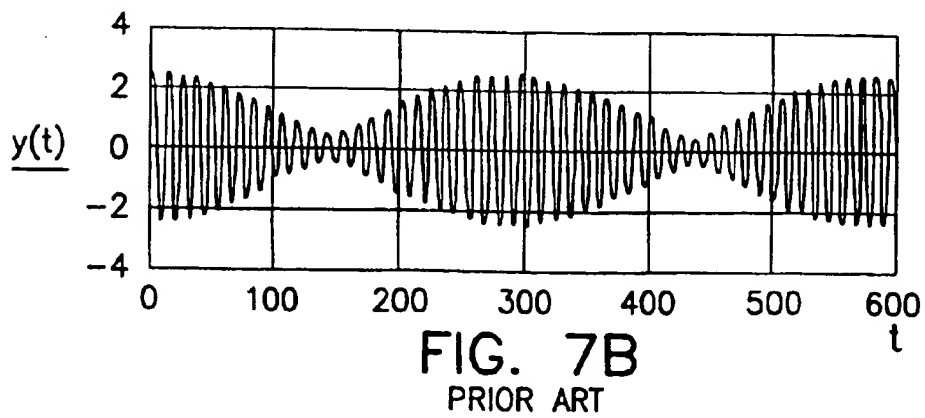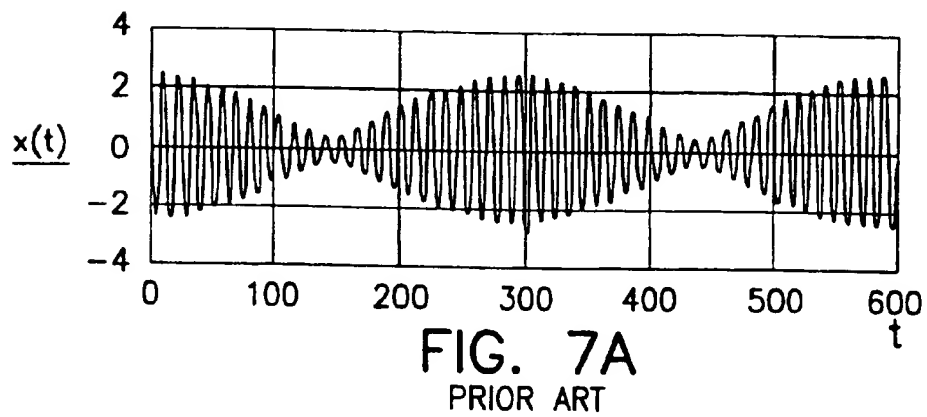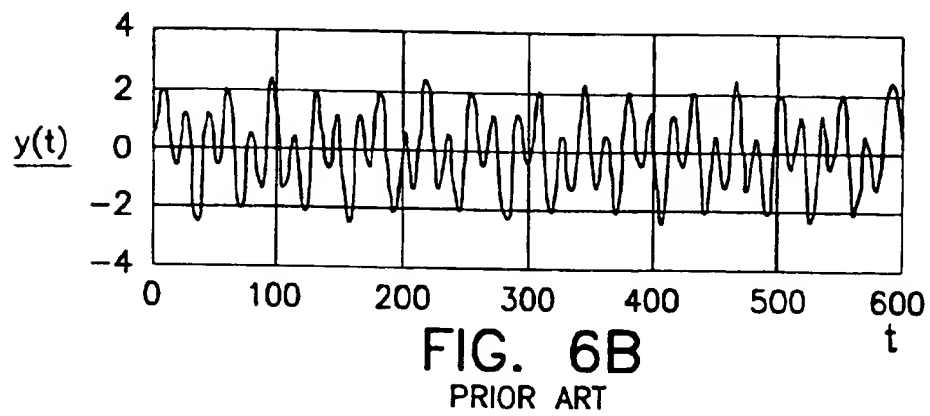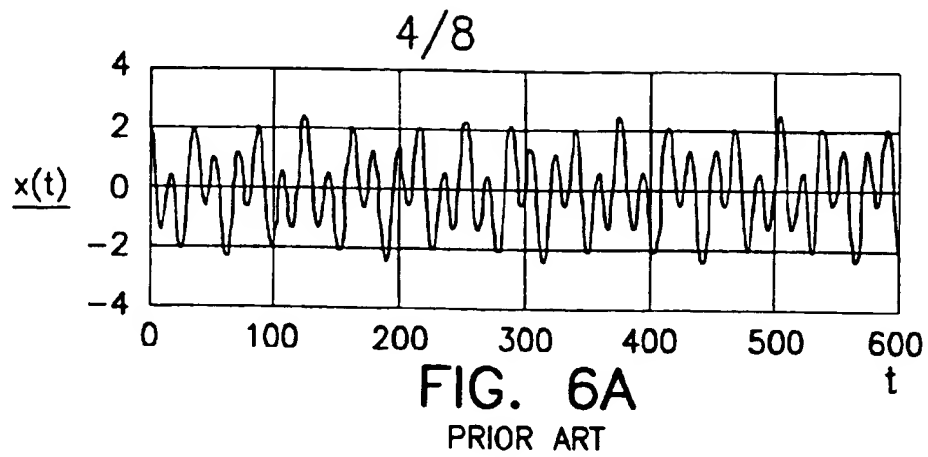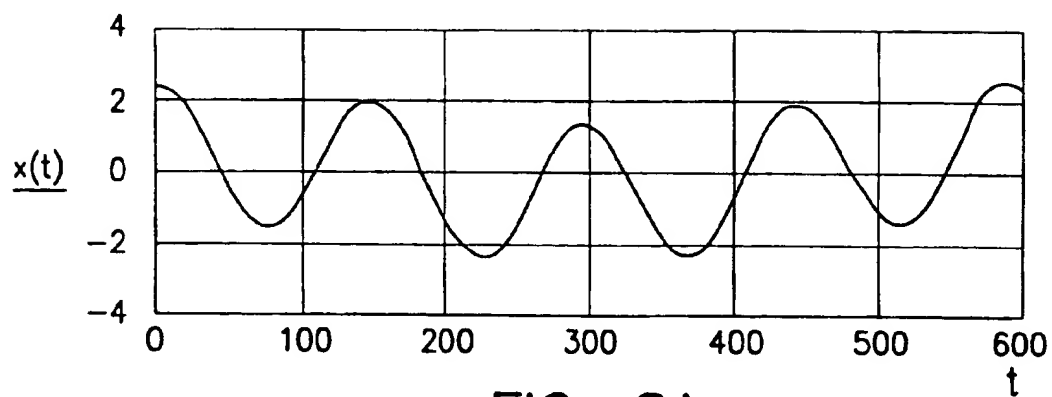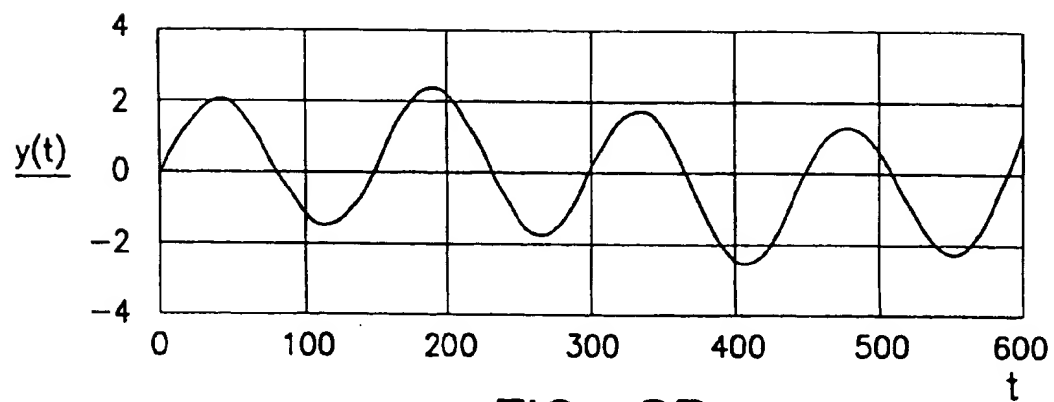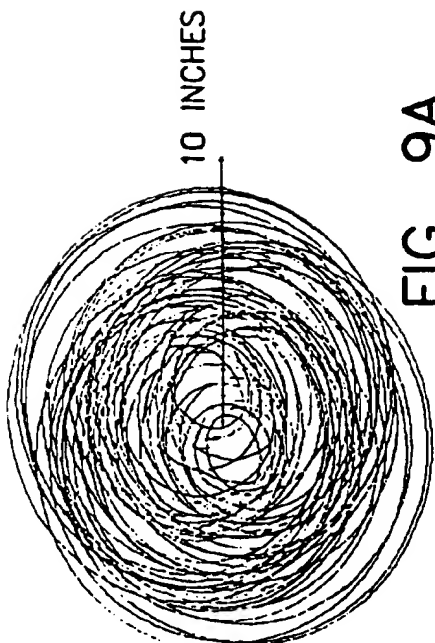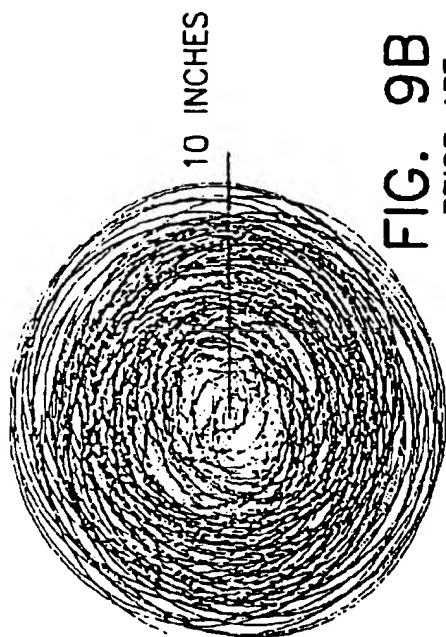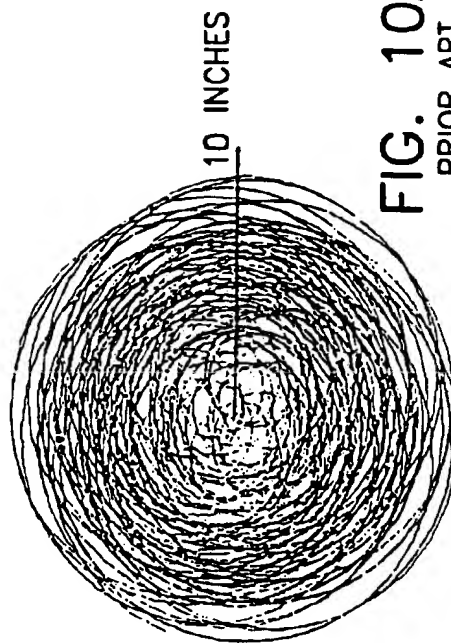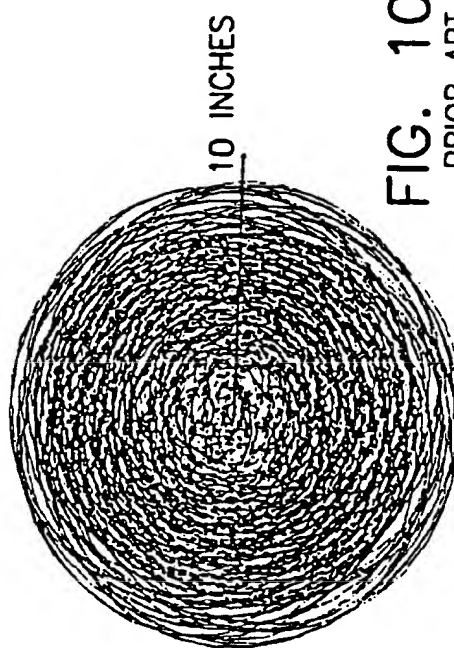
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FIG. 6A
PRIOR ART

FIG. 6B
PRIOR ART

FIG. 7A
PRIOR ART

FIG. 7B
PRIOR ART

FIG. 8A

FIG. 8B

10 INCHES

FIG. 9B
PRIOR ART

10 INCHES

FIG. 10B
PRIOR ART

10 INCHES

FIG. 9A
PRIOR ART

10 INCHES

FIG. 10A
PRIOR ART

10 INCHES

FIG. 11A

10 INCHES

FIG. 11B

+ BURNER 1

200

X

Y

100

+ BURNER 2

+ BURNER 3

FIG. 12
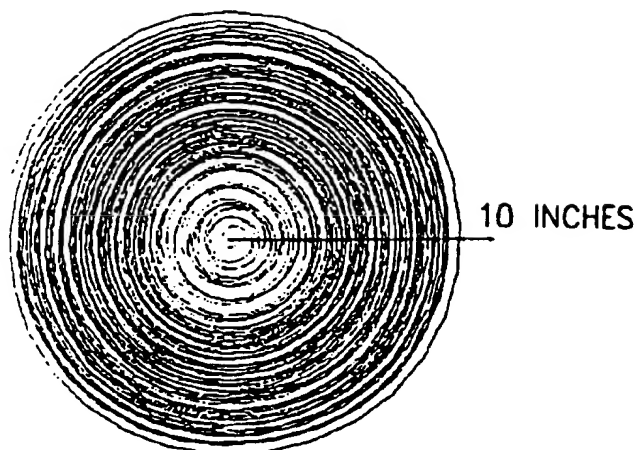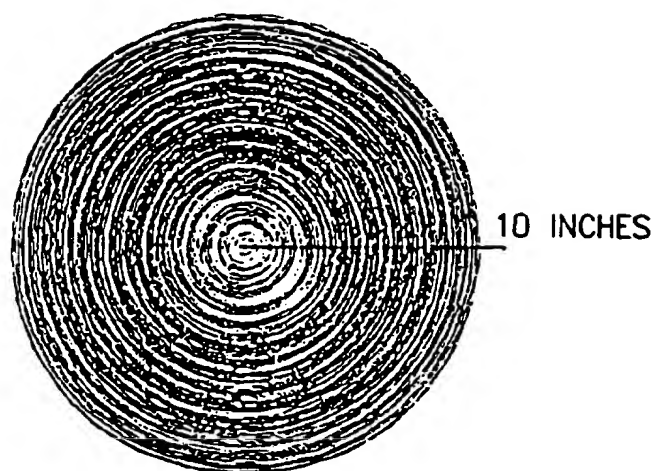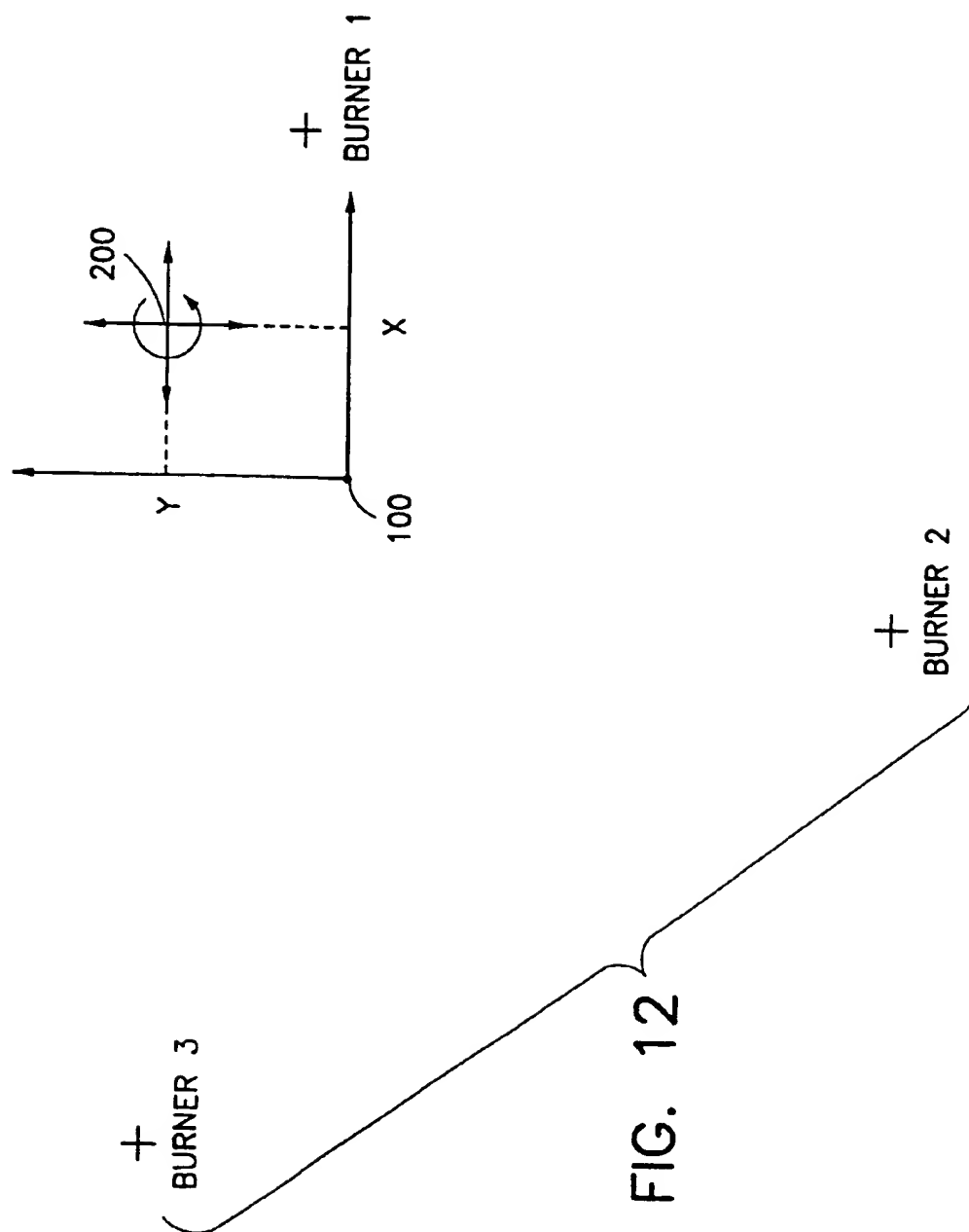
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C03C 3/06; C03B 19/00, 19/06, 37/018
US CL : 501/54; 65/17.4, 17.5

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/54, 900; 65/17.3, 17.4, 17.5, 414, 415, 416, 427

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, STN/CAS
search terms: hydrolysis, pyrolysis, silica, quartz, sio2, oscillat?, rotat?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- A	US 5,086,352 A (YAMAGATA ET AL) 04 February 1992, examples I, II and III.	12, 13, 27-29 ---- 1-11, 14-26, 30-38
Y	US 5,049,175 A (ROSS ET AL) 17 September 1991, col. 4, lines 30-36; col. 6, lines 6-63; col. 7, lines 1-44; col. 8, lines 1-5.	1-29
Y	US 4,363,647 A (BACHMAN ET AL) 14 December 1982, col. 6, line 23 to col. 7, line 36; figs. 3-5.	1-29
A	US 5,364,433 A (NISHIMURA ET AL) 15 November 1994, entire document.	1-38

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

Date of the actual completion of the international search	Date of mailing of the international search report
21 NOVEMBER 1996	12 DEC 1996

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